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(71) Applicant : **THE DOW CHEMICAL COMPANY (a Delaware corporation)**
2030 Dow Center Abbott Road
Midland Michigan 48640 (US)

(72) Inventor : **Leugers, Mary Anne**
2659 Brown Wood Trail
Midland, Michigan 48642 (US)
Inventor : **Mills, Michael Edward**
604 Sylvan Lane
Midland, Michigan 48642 (US)

(74) Representative : **Peuscet, Jacques et al**
Cabinet Peuscet 68, rue d'Hauteville
F-75010 Paris (FR)

(54) Probe for photoacoustic analysis.

(57) A probe (15) for quantitative detection of the concentration of an analyte in a sample (12) includes a hollow elongated body (14) adapted for single ended contact with the sample. The body (14) has at least one optical fiber extended through the body (14) for transmitting modulated light (26) through the body (14), out a window at the forward end of the body (14), and along an optical axis (25) into the sample (12) to optically excite the analyte. A pressure transducer (34) mounted beyond the window and spaced laterally away from the optical axis (25) detects an acoustic response of the analyte to the modulated light. This probe is particularly suitable for performing remote photoacoustic analysis of analyte concentration in a sample.

Jouve, 18, rue Saint-Denis, 75001 PARIS

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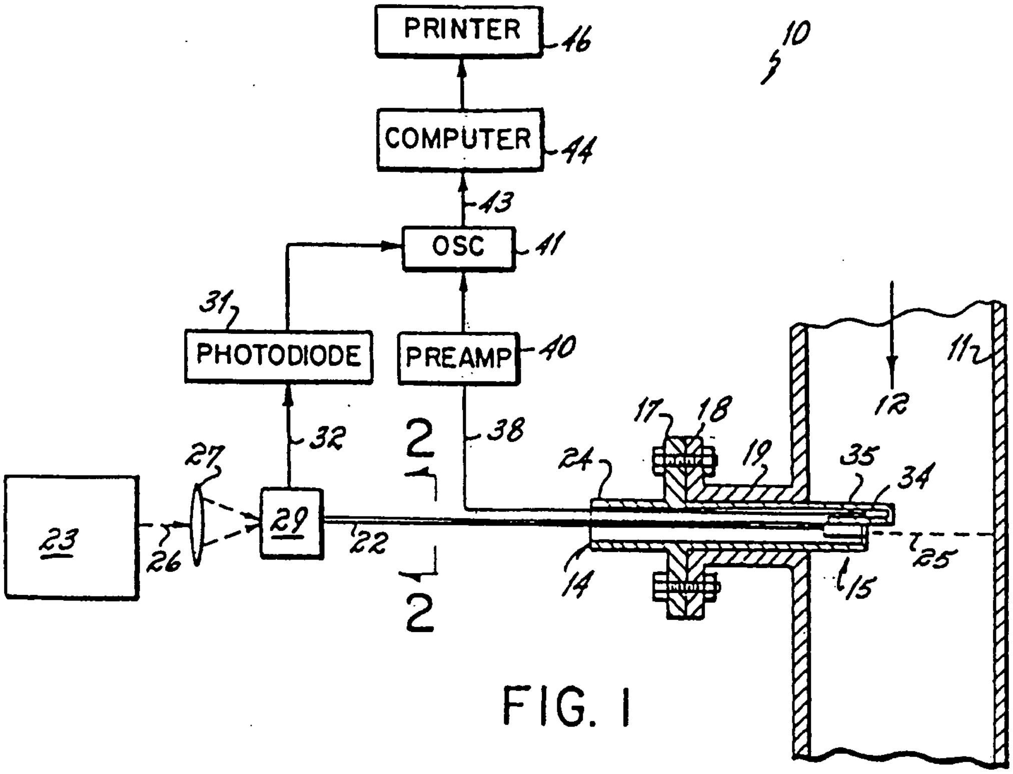

FIG. 1

This invention relates to a probe for optically exciting a sample and then detecting the photoacoustic response of a light absorbing analyte in the sample.

In many industrial applications, it is necessary to detect a concentration of an analyte in a sample, the sample being a liquid, gas or solid and the concentrations ranging from parts per billion to 100%. This invention relates to the remote detection and subsequent quantitative analysis that is necessary to determine the concentration of an analyte in a sample. Remote detection and analysis is typically necessary when, due to the chemical makeup of the sample or the commercial application for the analyte, intrusive or invasive detection and analysis would be either impractical or dangerous.

One method of detecting concentrations of an analyte in a sample is referred to as photoacoustic analysis. In photoacoustic analysis, the concentration of an analyte in a sample is determined by measuring the acoustic response of the sample after excitation by a modulated incident light of known wavelength. The magnitude of the acoustic response is a function of the concentration of the analyte within the sample. As the concentration of an analyte within the sample increases, an acoustic response of greater magnitude is detected. By establishing a reference magnitude for a known concentration(s) of a particular analyte in a particular sample, other unknown concentrations of the same analyte and sample can be subsequently determined.

There are a number of practical limitations associated with photoacoustic detection of an analyte in a sample, particularly if the sample is flowing liquid or gas. For instance, it can be extremely difficult to direct a modulated incident light into a flowing sample in a manner which produces an interference-free photoacoustically detectable signal or response. Many attempts to provide a sufficiently interference free signal involve routing of the sample through an isolated chamber and then returning the sample to its normal flow path, with optical excitation and photoacoustic detection occurring in the chamber. This enables detection of a component concentration in a liquid sample while it is in a flowing state. U.K. Patent Application No. 2,089,041A discloses such a device. Also, see United States Patent 3,938,365.

For many volatile and/or dangerous solutions, tapping into a sample line or pipe and rerouting the flow path of the sample in this manner can be cumbersome and/or expensive. However, unless the sample can be isolated in this manner, or in a similar manner, it is difficult to coordinate the directing of modulated light into the sample in a manner that will produce an interference-free photoacoustic response signal.

It is therefore an object of this invention to provide an improved apparatus for remotely directing modulated light into a sample to photoacoustically detect low concentrations of an analyte within the sample.

It is another object of the invention to provide an apparatus for non-invasive, interference free photoacoustic detection of the concentration of an analyte in a volatile and/or dangerous sample without requiring sample rerouting or removal.

It is still another objective of the invention to provide a relatively inexpensive, improved apparatus for effectively and conveniently coordinating optical excitation and acoustic detection of a sample in order to quantitatively measure low concentrations of an analyte in the sample.

In particular, the invention is a photoacoustic analysis probe, comprising: (1) a body, the body being hollow and having a forward end; (b) a window, the window being sealed to the body near the forward end of the body; (c) an optical fiber, the optical fiber extended into the body and terminating within the body near the window so that modulated light can be directed along the optical fiber, through the window and then along an optical axis extending from the window and through a sample surrounding the forward end of the body; characterized by (d) means for photoacoustic detection located within the body and adjacent the optical axis for detecting an acoustic response of the sample to the modulated light.

Fig. 1 is a schematic showing the components of a photoacoustic analysis system in accordance with a preferred embodiment of the invention;

Fig. 2 is a cross-sectional view taken along line 2-2 of Fig. 1;

Fig. 3 is an enlarged view of a single ended probe depicted in Fig. 1; and

Fig. 4 is a cross-sectional view taken along lines 4-4 of Fig. 3.

Fig. 1 illustrates a preferred embodiment of the invention comprising a photoacoustic detection system 10 useful for determining the concentration of an analyte in a liquid sample 12 flowing through a pipe 11, for example. For this purpose, one end of a probe 15 is placed directly in contact with the sample 12. The probe 15 includes an elongated, hollow body 14 with a length of about 30 centimeters. According to this embodiment, the probe 15 includes a flange 17 bolted to a corresponding flange 18 of an outlet port 19 in the pipe 11. During times when analysis is not taking place, the probe 15 may be withdrawn and outlet port 19 capped off, or plugged in any suitable manner to prevent leakage.

During analysis, light directed from a flash lamp 23 initially follows a path indicated by directional arrow 26 onto a lens 27, preferably a 25.0 milimeter (mm) plano-convex silica lens. This lens 27 focuses the light upon a wide bandpass 225 nanometer filter 29. Some of the light is conveyed via a fiberoptic cable 22 through a rearward end 24 of the body 14, through a window (not shown in Fib. 1) located at the forward end of the probe 15, and into the sample 12 along an optical axis 25. Fig. 2 is a cross-sectional view of the cable 22 and shows three optical fibers 22a. Referring again to Fig. 1, a portion of the light from the source 23 is also conveyed by an optical fiber or cable 32 to a photodiode 31, which is connected to an input of one of the vertical channels of an oscilloscope 41. Preferably, a bifurcated cable is used, with the trunk end of the cable connected to filter 29 and cable 32 serving as one branch for directing modulated light to photodiode 31 and cable 22 serving as the other branch for directing the modulated light to the probe 15. The filter 29 prevents individual fibers of cables 22 and 32 from degrading due to prolonged UV exposure. The individual fibers of the fiber cables 22 and 32 may be of various diameters. Moreover, cables containing any number of optical fibers may be used, although a single optical fiber with a single insulation tube seems to provide optimum results.

The flash lamp 23 may be a short arc (3 mm) Xenon flash lamp. Flash durations of 10 microseconds may be obtained by discharging 5.5 joules of energy to the bulb of the flash lamp 23 from an external 12 microfarad capacitor (not shown) charged to 950 volts. A square wave generator may be used to send trigger pulses to the flash lamp 23. Trigger pulses with a 5.0 volt amplitude, a 200 microsecond duration, and 200 millisecond delay times can be used. Typical flash rates of 3-5 Hertz (Hz) may be achieved by setting the frequency dial of the square wave generator to 0.15 - 0.25 x 10^4 kHz.

The directing of modulated light into the sample generates a sound wave or pulse in a light absorbing analyte within the sample. The sound waves are detected by a pressure transducer 34, preferably a piezoelectric detector, which is located beyond the window and spaced laterally away from the optical axis 25.

In response to acoustic detection, the transducer 34 generates an electrical signal that is relayed through the body 14 by an electrical lead 38 for input into a preamplifier 40. The amplified signal is then inputted to another of the vertical channels of the oscilloscope 41. A voltage corresponding to the acoustically detected response can be displayed and measured on the oscilloscope 41, and subsequently transmitted via an electrical cable 43 to a computer 44. If desired, the time varying voltage may be recorded or stored by the computer 44 and subsequently printed by a printer 46 connected to the computer 44.

The acoustically detected waveforms obtained from the probe 15 typically comprise several superimposed frequencies that are proportional to the pipe 11 dimensions or the dimensions of a cell which holds the sample. The amplitudes of the high frequency (150 kHz) acoustically detected waveforms may be used for concentration measurements by normalizing these waveforms against the amplitude of the photodiode-generated electrical signal.

Fig. 3 depicts, in greater detail, a preferred embodiment of the forward end of the probe 15. A cap 35 is located at the forward end of the probe 15. The cap 35 may be integrally formed with the body 14 or simply connectable thereto. Preferably, both the cap 35 and the body 14 are of stainless steel, and the cap 35 is threadably connected to the body 14. A window or lens 40a is located in the center of the cap 35 in alignment with optical axis 25. The lens 40a is preferably plano convex in shape, made of sapphire and has a thickness of about 5 mm with a focal length of about 9 mm. The lens 40a reduces light beam divergence, or collimates the light, as it is directed into the sample. The cap 35 also includes a longitudinal, hollow, annulus portion 47 that extends beyond the lens 40a and which houses the transducer 34. The annulus portion 47 has a longitudinally extending inner wall 48 and an outer wall 49. Preferably, the annulus portion 47 has a longitudinal dimension of about 15 mm, and the radial distance between the wall 48 and the wall 49 is about 8 mm. This places the inner wall 48 a radial distance of about 5 mm from the optical axis 25.

As shown more clearly in Fig. 4, the piezoelectric transducer 34 is mounted flush against a backside surface 50 of the inner wall 48, and is oriented perpendicular to optical axis 25, thereby optimizing acoustic sensitivity. The transducer 34 is preferably held against back side surface 50 by a leaf spring 65. The transducer 34 is also mounted to a lead backing 51 that is connected to an electrical lead 38 which extends along the length of the probe body 14 and out rearward end 24. In order to measure a voltage, or a potential difference with respect to ground, a second lead (not shows) serves as the ground reference and is connected separately to an outer surface 52 of the probe body 14.

The fiberoptic cable 22 extends through the body 14 into a hollow mounting ring 55 which is frictionally held on its external surface by another ring 56 that threadably connects within a core section 58 of the cap 35. The sapphire lens 40a is held in place by a circular flange 49 at the forward end of core 58 and by two O-rings, 60 and 61. This overall structure places the lens 40a about 9 mm, i.e., its focal length, from the end of cable 22, and it also prevents sample leakage into the probe body 14. Moreover, O-rings 60 and 61 acoustically isolate the light delivery system to substantially reduce adverse effects that may otherwise be caused by undesired photoacoustic detection of scattered light transmitted through the fiber bundle 22.

Although the probe 15 as shown in Fig. 1 is adapted for in-line photoacoustic analysis of a liquid sample flowing through the pipe 11, it is to be understood that the forward probe end could also be placed directly in a nonflowing pool of the liquid sample, or the probe body 14 mounted to an enclosed, sample holding device or cell. Additionally, the forward probe end could be positioned in contact with either a solid sample or a gas sample. In the case where a gas sample is to be monitored, as in smokestack emissions, a microphone would be the preferred pressure transducer rather than the piezoelectric sensor.

Moreover, it is understood this invention also contemplates various other acoustic and sensor configurations. One advantage associated with the particular embodiment of the invention shown in Figs. 1, 3 and 4 relates to the fact that the acoustic sensor geometry substantially matches the optically-generated acoustic wave geometry. That is, the semicircular shape of the sensor places all points on its surface substantially equidistant from the optical axis traversed by the light beam, thereby maximizing sensitivity. Nevertheless, numerous other geometric orientations of the acoustic sensor with respect to the optical axis would be suitable, and within the scope of the claims.

While a preferred embodiment of the invention has been described, other modifications and advantages will become readily apparent to one of ordinary skill in the art without departing from the scope of the invention, and applicant intends to be bound only the claims appended hereto.

Claims

1. A photoacoustic analysis probe (15), comprising
   (a) a body (14), the body (14) being hollow and having a forward end;
   (b) a window (40a), the window (40a) being sealed to the body (14) near the forward end of the body (14);
   (c) an optical fiber (22a), the optical fiber (22a) extended into the body (14) and terminating within the body (14) near the window (40a) so that modulated light (26) can be directed along the optical fiber (22a), through the window (40a) and then along an optical axis (25) extending from the window (40a) and through a sample (12) surrounding the forward end of the body (14); characterized by
   (d) means for photoacoustic detection (34) located within the body (14) and adjacent the optical axis (25) for detecting an acoustic response of the sample to the modulated light.

2. The probe (15) of Claim 1, wherein the means for photoacoustic detection (34) has a longitudinal axis that is parallel with the optical axis (25).

3. The probe (15) of Claim 2, wherein the means for photoacoustic detection (34) is a pressure transducer.

4. The probe (15) of Claim 2, wherein the means for photoacoustic detection (34) is a microphone.

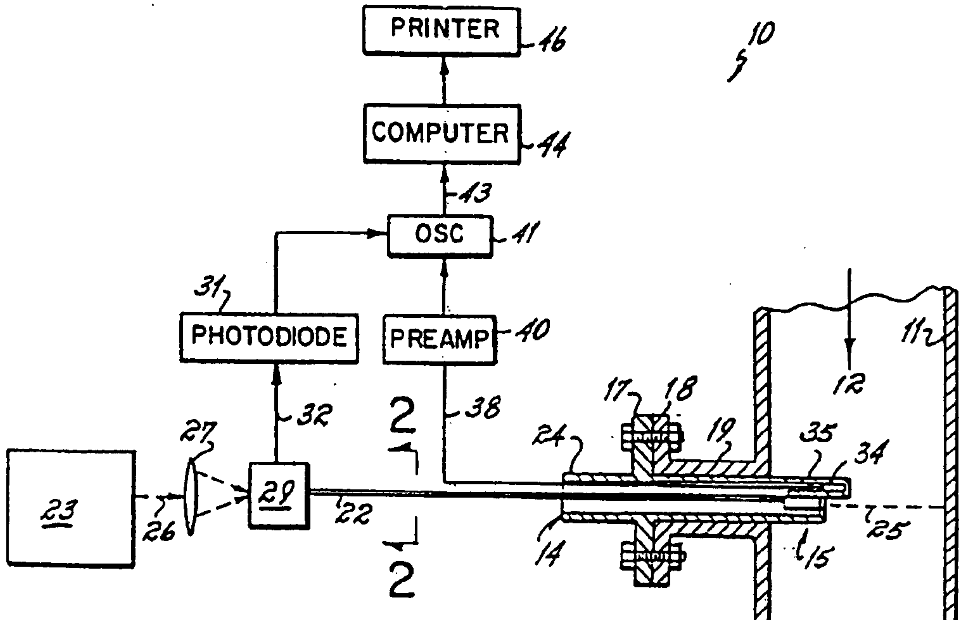

FIG. 1

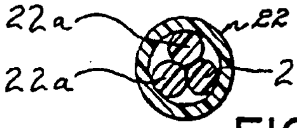

FIG. 2

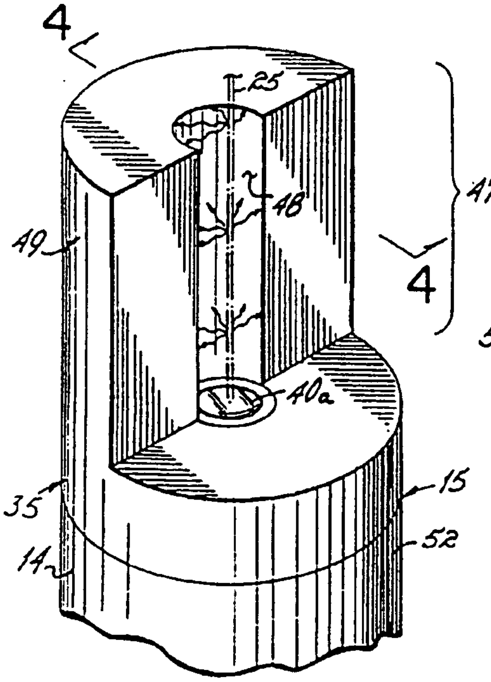

FIG. 3

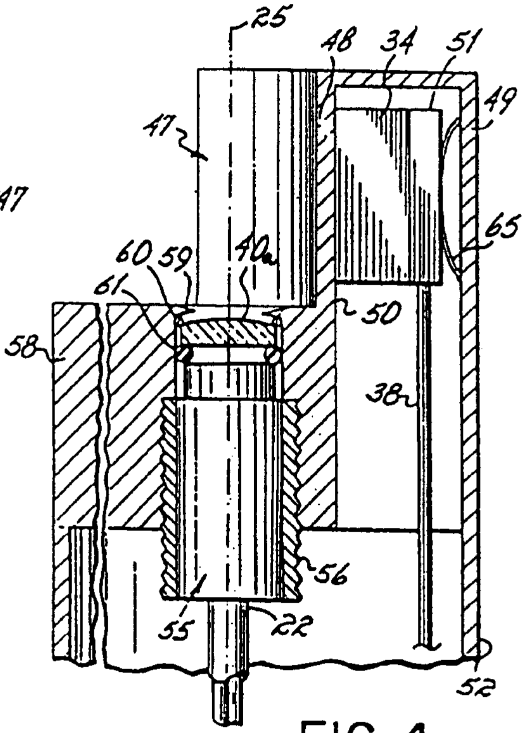

FIG. 4

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EUROPEAN SEARCH REPORT

Application Number

EP 91 40 2400

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
A	GB-A-2 218 198 (MINE SAFETY APPLIANCES CO.) * pages 1,2 * ---	1,3,4
A	EP-A-0 286 419 (N. MCMILLAN) * column 2, lines 17-30; column 7, lines 17-21 * ---	1,3,4
A	MEDICAL & BIOLOGICAL ENGINEERING & COMPUTING vol. 23, no. 6, November 1985, pages 585-588, London, GB; P. POULET et al.: "In vivo cutaneous spectroscopy by photoacoustic detection" * figure 2 * ---	1
A,P	REVIEW OF SCIENTIFIC INSTRUMENTS vol. 61, no. 12, December 1990, pages 3729-3732, New York, US; R.E. RUSSO et al.: "Remote photoacoustic measurements in aqueous solutions using an optical fiber" * figure 1 * ---	1
A,D	US-A-3 938 365 (C.F. DEWEY) * abstract * ---	1
A,D	GB-A-2 089 041 (TOYO SODA MANUFACTURING CO. LTD.) * abstract * -----	1

CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
G 01 N 21/17

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
G 01 N G 01 H A 61 B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	14-01-1992	BRISON O.P.

CATEGORY OF CITED DOCUMENTS

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